

Effects of Tetrahydrofuran as a Structure Modifier in Preparation of SBS Thermoplastic Block Copolymers in Cyclohexane

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SYNOPSIS

Linear styrene-butadiene block copolymers of polyA-*block*-polyB-*block*-polyA type (SBS) were synthesized in the presence of varying amounts of THF functioning as the polar structure modifier. The efficiency of this modifier was studied by analyzing the microstructure of synthesized polymers using ^{13}C -NMR, and the effect of THF on polymerization kinetics was determined by progressive buildup of the molecular weight measured by GPC. Polymerization at 4000 ppm THF concentration resulted in the highest styrene polymerization rate while a 1 wt % concentration gave the highest butadiene polymerization rate. The vinyl content increased from 20 to 64% with an increase in the amount of THF from 200 ppm to 1 wt % while the content of *trans*-1,4 and *cis*-1,4 units decreased. For SBS polymer synthesized via a sequential process, the use of THF as the structure modifier enhanced the crossover efficiency that would otherwise result in a skewed molecular weight distribution with a higher polydispersity. For SBS polymer made via a coupling process, the coupling efficiency decreased when the amount of THF exceeded a certain limit. The temperature dependence of the coupling efficiency was also investigated. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Styrene-butadiene block copolymers of polyA-*block*-polyB-*block*-polyA type (SBS) have been traditionally made via either a sequential method, wherein the three blocks are formed sequentially using a monoanionic organolithium compound as the initiator, or a coupling method, wherein diblock precursors are linked by a coupling agent leading to the formation of a final polymer.^{1,2} The resulting polymer constitutes an important class of thermoplastic elastomers. However, this SBS block copolymer does not have good long-term heat, weather, and UV stability due to the presence of a large amount of unsaturated aliphatic double bonds in the polybutadiene segment. As a result, hydrogenation (saturation) was used to improve the stability. To keep the hydrogenated SBS copolymer from crystallizing and losing its elastomeric properties, the microstructure

of the polybutadiene segment must be modified, prior to the hydrogenation, by raising the 1,2-polybutadiene (vinyl) content relative to the 1,4-polybutadiene.³⁻⁵ This could be achieved by using polar species to effect the isomerization of the polydiene segment during the copolymer synthesis. These polar species are primarily Lewis bases including ethers, amines, ketals, and orthoesters.⁶⁻⁹ Extensive studies were made in the early 1950s-1970s reporting the use of various initiators in a variety of polar solvents.¹⁰⁻¹⁸ Recent reviews have been made by Morton,¹ Young et al.,¹⁹ and Van Beylen et al.²⁰ on topics such as the modifying powers for various organometallic initiators in polar solvents, the kinetics of polymerization, and the isomerization mechanism occurring at the carbon-metal bond at the tip of the growing chain. Nevertheless, most of these microstructure studies were carried out on homopolydienes such as polybutadiene and polyisoprene. In addition, while studies in bulk polar ethers abound, very few studies have been made on nonpolar solvents containing small amounts of polar ethers. Among these few studies, Bywater and Worsfold^{13,15}

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investigated the influence of THF on polymerization of styrene in benzene and found that the ratio of THF to initiator significantly affects the polymerization rate. Morton¹ found that aliphatic solvents led to a higher *cis*-1,4/*trans*-1,4 ratio than aromatic solvents with little effect on vinyl content and THF drastically altered the microstructure of polybutadiene from high 1,4- to high 1,2-content, even when a very small amount was added to the nonpolar solvent. Recently, renewed interest in tailor-made polymer architecture has prompted new microstructure studies. Van der Velden and Fetters²¹ determined the microstructures of anionically prepared polybutadienes, either deuterated or nondeuterated, using ¹³C-NMR. Chang and coworkers²² studied the anionic polymerization of butadiene using tetramethylethylenediamine (TMEDA) as the modifier in hexane with TMEDA to *n*-BuLi molal ratio ranging from 0 to 3.5. Halasa et al.²³ studied the solution polymerization of styrene-butadiene random copolymers and found each polybutadiene microstructure approached respective limiting values at around a TMEDA to *n*-BuLi ratio of 2. Hsu and Halasa²⁴ discovered that salts of tetrahydrofurfuryl alcohols could be used to modify anionic polymerization of conjugated diene monomers. By selecting proper ratios of potassium 2-methyl-2-butoxide (*t*-AmOK) and THF to *n*-BuLi, Bu and Ying^{25,26} obtained styrene-butadiene (SB) copolymers with unique randomness. Hergenrother and colleagues²⁷ found that the 2,1-addition predominated when adding a small amount of polar modifier during the random copolymerization of styrene and butadiene using trialkyltin lithium as the initiator. Among all these studies, analysis regarding the optimal use of THF as a structure modifier, as well as its effect in the preparation of SBS block copolymers in cyclohexane, was lacking. In view of the fact that SBS copolymers in commercial processes are typically made in cyclohexane solvent, the purpose of this work was to conduct systematic studies in such a system to gain more detailed information.

EXPERIMENTAL

Materials

Butadiene, styrene, and cyclohexane used in this work were obtained from Taiwan Synthetic Rubber Corp. (TSRC). The butadiene was vaporized, recondensed, and treated with activated alumina (from Alcoa Co.) to remove any impurities, moisture, and the inhibitor. The styrene was washed with 10% NaOH solution followed by activated alumina

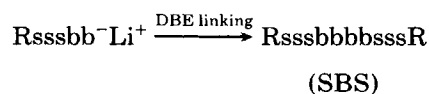
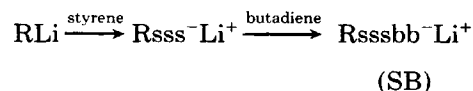
treatment to remove the inhibitor. *n*-Butyllithium at 15 wt % concentration was purchased from Merck. Reagent grade THF (BDH, 99.7% purity) was pretreated with activated alumina. 1,2-Dibromoethane (DBE) (Merck, 99% purity) was used as coupling agent and pretreated with activated alumina.

SBS Synthesis

In this work, the SBS copolymers were synthesized in two different ways: the coupling method and the sequential method.

Coupling Method

The SBS copolymer was prepared via anionic polymerization using *n*-butyllithium as the initiator and DBE as the coupling agent in cyclohexane solvent. The experiments were conducted in an air-free glass autoclave (Taiatsu, Japan). To begin a polymerization experiment, an appropriate amount of cyclohexane was put into a 1-L pressure vessel. The vessel content was heated to 40°C prior to the addition of the required weight of the structure modifier and *n*-butyllithium. A required amount of styrene was then charged into the reactor. Anionic propagation occurred and the solution turned red indicating the formation of the living polystyryllithium chain ends. Two to 5 min after the vessel temperature reached the maximum, the reaction content was cooled to 40°C. Afterward the butadiene was charged into the vessel to continue the polymerization, forming the polystyrene-*block*-polybutadiene diblock polymer. The color of the solution changed from red to yellow, indicating the formation of the living polystyrylbutadienyllithium chain ends. Two to 5 min after the vessel temperature reached the maximum, the solution was cooled and maintained at the desired temperature for the succeeding coupling reaction. DBE (with 25% in excess of the stoichiometry to maximize the degree of coupling) was charged to link the SB diblocks forming the final SBS copolymer. We allowed 30 min to complete the coupling reaction. The overall polymer synthesis reaction was as follows:



where R = *n*-butyl.

Table I Carbon Signal Determination of SBS Copolymer in ^{13}C -NMR Spectrum

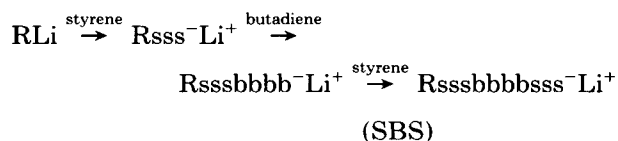
Chemical Shift (ppm)	Assignment
24.9	<i>cis</i> [γ effect]
27.4	<i>cis</i> -1,4
30.2	<i>trans</i> [γ effect]
32.6	<i>trans</i> -1,4
34.0	<i>cis</i> [β effect]
38.1	<i>trans</i> [β effect]
114	vinyl [=CH ₂]
125	styrene [<i>para</i> CH]

At the completion of the polymer synthesis, antioxidant (Irganox 1076) was added and the vessel content was poured into isopropanol and the SBS polymer precipitated. After drying in a vacuum oven, the polymer was analyzed for its molecular weight and microstructure.

Sequential Method

In this method the three blocks of the SBS copolymer were made sequentially. To make the same

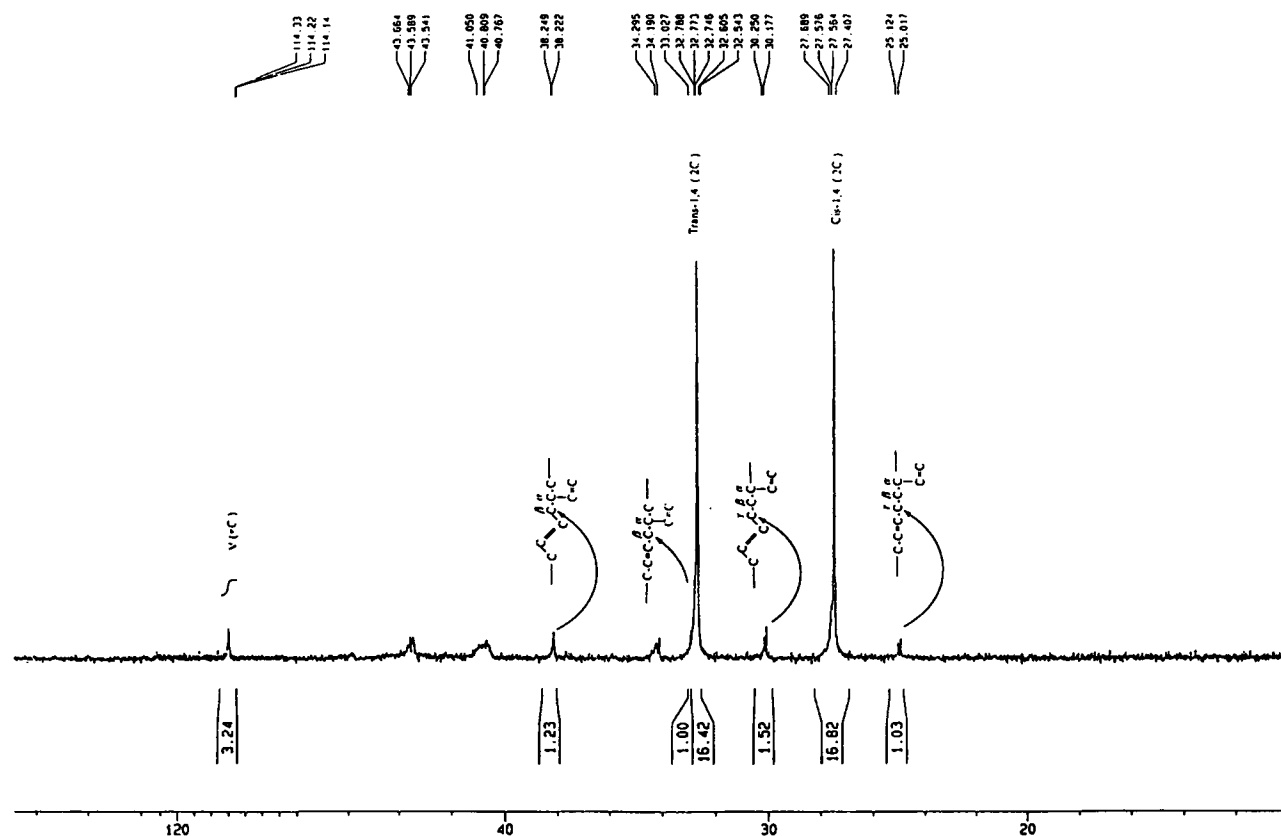
molecules as those from the coupling method, the *n*-butyllithium charge was reduced by half. In addition, half of the styrene charge was delayed until the butadiene polymerization was complete. No coupling agent was needed, but a small amount of methanol was added at the end to terminate the living styryllithium chains. Other experimental conditions remained the same as the coupling method. The overall polymer synthesis reaction was as follows:



where R = *n*-butyl.

Analysis of Synthesized Polymer

The molecular weights and molecular weight distributions of synthesized polymers were determined by a Waters gel permeation chromatograph (GPC) equipped with Waters M-486 adsorbance (UV) and Waters 410 differential refractive index (RI) detectors. The GPC was operated using three Waters UI-


Figure 1 ^{13}C -NMR spectrum of SBS copolymers.

trastyrigel columns (10^3 , 10^4 , 10^5 Å) at a nominal flow rate of 1 mL/min with a sample concentration of 0.1% in THF solvent. The GPC instrument was calibrated using monodisperse polystyrene standards. The microstructure was determined using the Bruker AMX400 100.61 MHz ^{13}C -NMR.

RESULTS AND DISCUSSION

Effect of Modifiers on Microstructure of Polybutadiene Segment

Although FTIR was convenient for identifying the various isomeric units of polybutadiene, a quantitative determination of the content of each of these isomers in the SBS copolymer usually incurred significant inaccuracy. This is because the overlapping of the polystyrene peak makes it difficult to distinguish the absorbance of *cis*-1,4 polybutadiene. As a result, using the Beer's law to calculate the contents of each isomeric unit based on absorbance coefficients^{28,29} would involve a relatively large error. Thus we used NMR in studying the microstructure of polybutadiene. Because it was difficult to distinguish the *cis*-1,4 and *trans*-1,4 microstructures in the ^1H -NMR spectra, ^{13}C -NMR was used. While it was straightforward to determine the relative portions of *cis*-1,4, *trans*-1,4, and vinyl microstructures for homopolybutadiene, the analysis for a random copolymer of butadiene and styrene was much more complicated.³⁰⁻³⁶ With the use of inverse gated ^1H decoupling ^{13}C -NMR, the content of each isomeric unit for the SBS block copolymers was calculated based on the absorption peaks of vinyl, *cis*-1,4, and *trans*-1,4 along with the chemical shifts (γ effect and β effect) of *cis*-1,4 and *trans*-1,4 caused by the vinyl unit.^{37,38} The peak assignment in a ^{13}C -NMR spectrum is shown in Table I. A typical spectrum is shown in Figure 1 and the contents of each isomeric unit were calculated as follows:

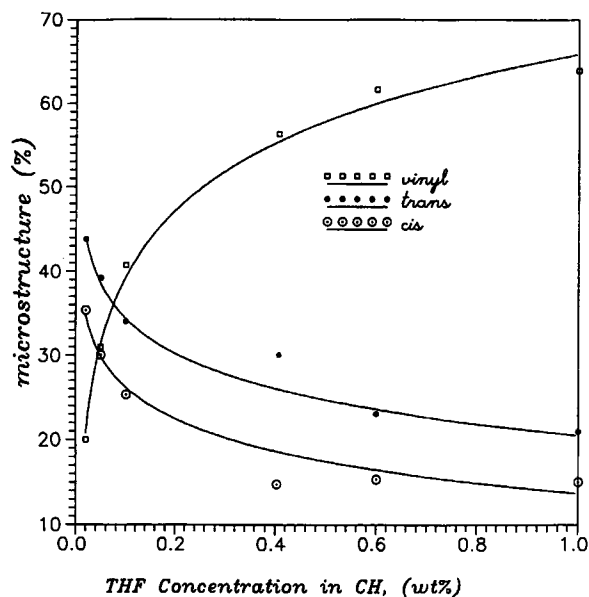


Figure 2 Microstructure of the SBS polymer at varying THF concentrations.

$$cis-1,4 = cis[\gamma \text{ effect}] + cis + cis[\beta \text{ effect}]$$

$$trans-1,4 = trans[\gamma \text{ effect}] + trans + trans[\beta \text{ effect}]$$

$$vinyl-1,2 = vinyl[=CH_2] \times 2.$$

After normalization, the percentage of each isomeric unit was readily determined. The effect of THF on the microstructure of the polybutadiene portion of the SBS copolymers is shown in Table II and Figure 2. The vinyl content increased from ~ 20 to $\sim 64\%$ with an increase in the amount of THF from 200 ppm to 1 wt % while the contents of *cis*-1,4 and *trans*-1,4 units decreased.

Effect of Polar Modifiers on Polymerization Rates

It is well known that the living styryllithium or butadienyllithium chain ends are associated in nonpolar

Table II Microstructure of SBS Polymers Using Varying Amounts of THF

THF	[THF]/[I] ^a	<i>trans</i> -1,4 (%)	<i>cis</i> -1,4 (%)	Vinyl-1,2 (%)
200 ppm	0.55	43.8	35.4	20.8
500 ppm	1.38	39.2	30.0	31.0
1000 ppm	2.76	34.0	25.3	40.7
4000 ppm	11.04	30.2	14.3	55.5
6000 ppm	16.56	23.0	15.3	61.7
1 wt %	27.60	20.4	15.5	63.9

Percent solids = 16.6%; *n*-BuLi initiator [I] = 3.9×10^{-3} mol/L; styrene [M] = 0.37 mol/L; butadiene [M] = 1.68 mol/L.

^a Molar ratio.

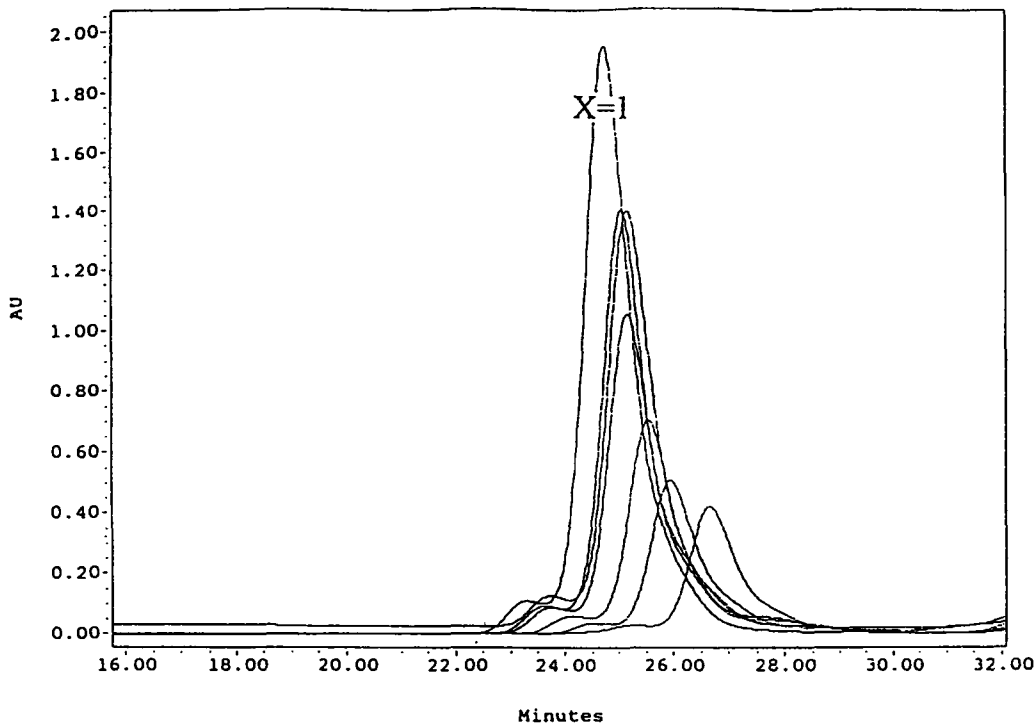


Figure 3 Progressive molecular weight increase during the polymerization.

hydrocarbon solvents.¹ This association phenomenon alters the kinetic mechanism and slows the polymerization rate. While the association does not occur in polar solvents due to their strong solvating power, the living chain end can exist in the form of a contact ion pair, loose ion pair, or free ions having different reaction rates. Therefore, in our reaction system, using the nonpolar cyclohexane as the solvent in the presence of 0.02–1 wt % of THF, the polymerization

rate varied with the amount of THF. To study the polymerization rates, isothermal experiments were carried out to synthesize homopolystyrene and homopolybutadiene under various modifier concentrations. The polymerizations were treated as a pseudo-first-order reaction as follows:

$$-\frac{d[M]}{dt} = k_{\text{obs}}[M]$$

where $[M]$ is the monomer concentration and k_{obs} is the apparent rate constant comprising the true rate constant and the concentration of living chain ends. At isothermal conditions, this equation integrates as

$$\ln \frac{[M]}{[M]_0} = -k_{\text{obs}}t$$

$$\ln(1 - X) = -k_{\text{obs}}t$$

where $[M]_0$ is the monomer concentration at $t = 0$ and X is the monomer conversion. The k_{obs} is then obtained from the plot of $-\ln(1 - X)$ versus t .

In our studies, the conversion, X , was calculated based on the progressive molecular weights measured from GPC as shown in Figure 3 in the following manner:

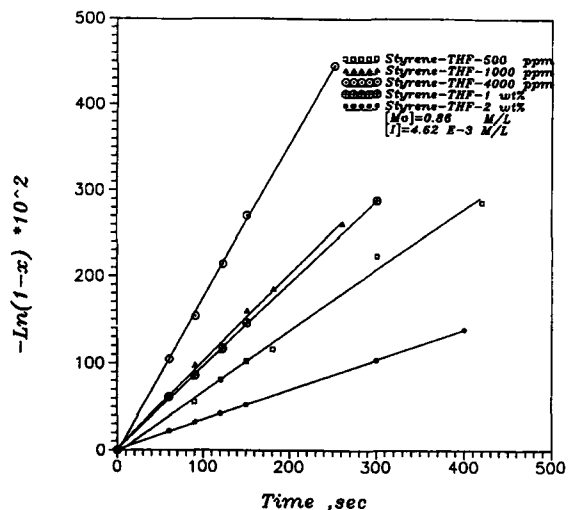


Figure 4 Conversion data for polymerization of styrene at 40°C with varying amounts of THF.

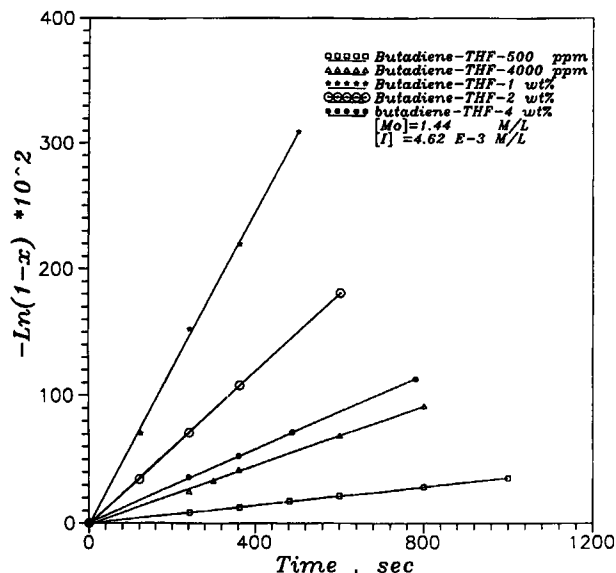


Figure 5 Conversion data for polymerization of butadiene at 40°C with varying amounts of THF.

$$X = 1 - \frac{[M]}{[M]_0} = \frac{MW}{MW_f}$$

where MW is the GPC molecular weight at time t , and MW_f is the molecular weight at the completion of polymerization. This method was justified due to the fact that the conversion factor between the actual molecular weight and the GPC molecular weight remained constant for the homopolymers.^{39,40}

The experimental data of polymerization of styrene and butadiene at 40°C using various amounts of THF as the modifier are shown in Figures 4 and 5, respectively. For polystyrene the rate increased as the THF concentration increased from 500 to 4000 ppm. Nevertheless, a further increase in the THF resulted in a rate decrease. A similar situation was observed for the polymerization of butadiene.

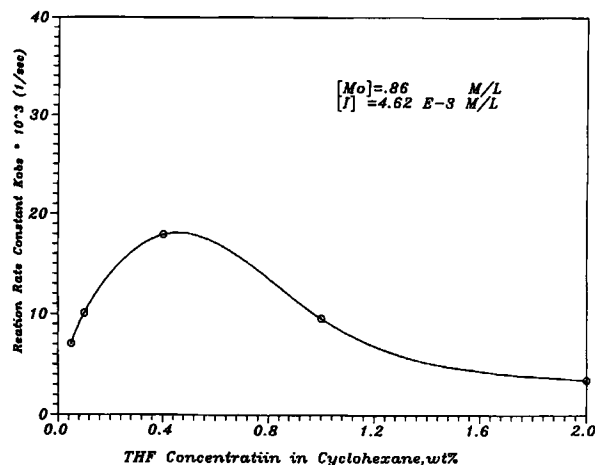


Figure 6 Rate constant for polymerization of styrene at 40°C with varying amounts of THF.

The rate increased with an increase in THF concentration from 500 ppm to 1 wt % and then decreased when THF was further increased. The corresponding rate constants are tabulated in Table III and plotted in Figures 6 and 7. The decrease in propagation rates of styrene and butadiene at high THF contents was surprising and probably could be attributed to the overcomplexation of THF with polymeric chain ends under our experimental temperatures. Albeit the above analyses were done under 40°C isothermal conditions, the observed rate change caused by the polar modifier was equally true even under a nonisothermal condition. The temperature profiles for nonisothermal polymerization of polystyrene and polybutadiene are shown in Figures 8 and 9, respectively. The effect of THF modifier on the rate of polymerization, reflected by these temperature profiles, was consistent with our previous observation under isothermal conditions. Thus, for making SBS copolymers, the amount of

Table III Rate of Polymerization Using Varying Amounts of THF at 40°C

Solvent		Polymerization of	
Nonpolar	THF	Styrene (K · 10 ³ , s ⁻¹)	BD (K · 10 ³ , s ⁻¹)
Cyclohexane	500 ppm	7.051	0.351
Cyclohexane	1000 ppm	10.079	—
Cyclohexane	4000 ppm	17.9	1.156
Cyclohexane	1 wt %	9.56	6.204
Cyclohexane	2 wt %	3.456	3.025
Cyclohexane	4 wt %	—	1.446

n -BuLi initiator $[I] = 4.62 \times 10^{-3}$ mol/L; for styrene homopolymerization $[M] = 0.86$ mol/L; for butadiene homopolymerization $[M] = 1.44$ mol/L.

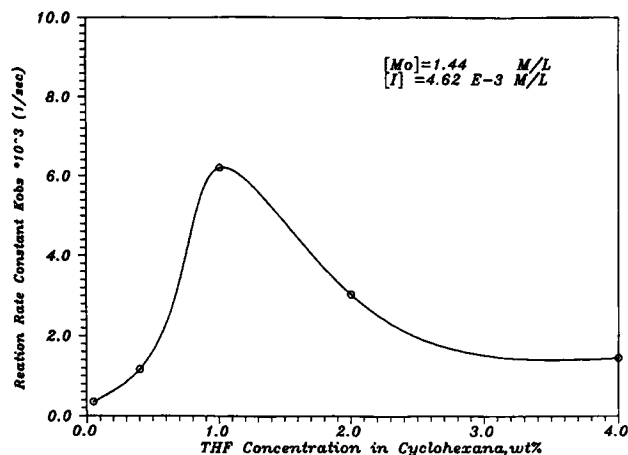


Figure 7 Rate constant for polymerization of butadiene at 40°C with varying amounts of THF.

THF should be between 4000 ppm and 1 wt % in order to achieve the maximum polymerization rates.

Crossover Efficiency in Sequential Polymerization of SBS

In the sequential SBS polymerization process, the polystyrene block was made first, followed by the addition of butadiene to the living polystyryllithium chain end. Polymerization of butadiene constituted the central block. The preparation of SBS copolymer was finally completed by the further addition of a second quantity of styrene, in an equal amount to the first styrene usage, to the living polystyrylbutadienyllithium chain end. However, the addition of styrene to the living polystyrylbutadienyllithium chain end was slow compared to the styrene-styrene

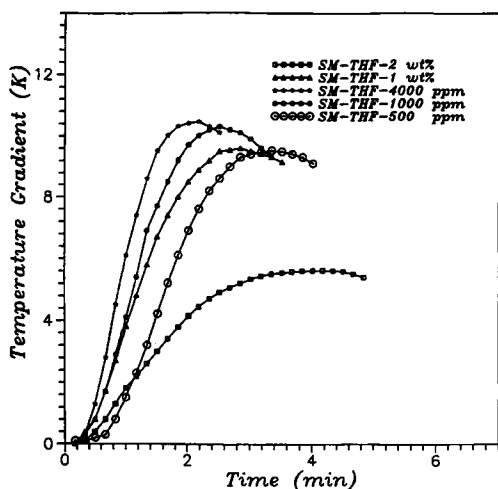


Figure 8 Temperature profiles for polymerization of styrene starting at 40°C with varying amounts of THF.

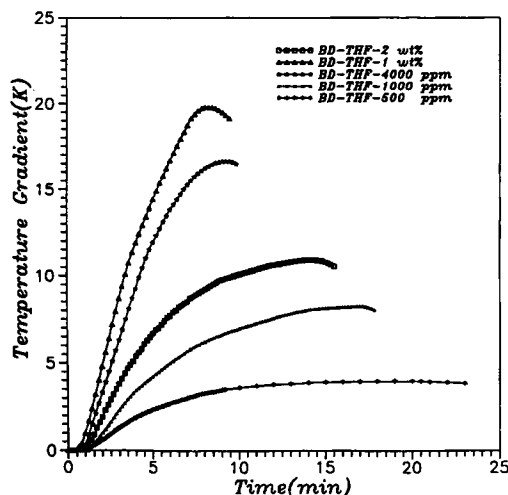


Figure 9 Temperature profiles for polymerization of butadiene starting at 40°C with varying amounts of THF.

propagation reaction.⁴¹ This low crossover rate resulted in a skewed third block molecular weight distribution and a higher polydispersity as shown in Figure 10. This deficiency overshadowed the edge of the narrower molecular weight distribution that the sequential method usually had on the coupling method. However, this crossover deficiency was circumvented by adding a small amount of polar solvent at the completion of the formation of the polybutadiene block.⁴² For the sequential polymerization conducted in our work, the THF, which was added for microstructure control of the polybutadiene block, was present from the beginning. This polar ether increased the rate at which styrene added to

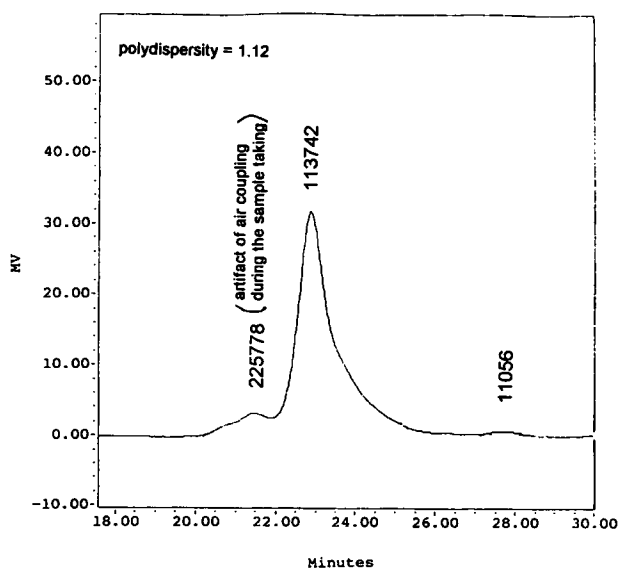


Figure 10 A skewed molecular weight distribution of SBS polymer made via a sequential method.

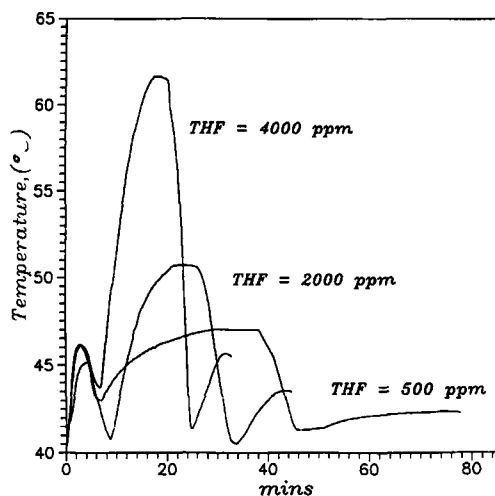


Figure 11 Temperature profile of a sequential polymerization of SBS polymer with varying amounts of THF.

the living polystyrylbutadienyllithium chain end relative to the styrene-styrene addition. Such enhancement in crossover rate can be best shown in the temperature profile of the reaction. As depicted in Figure 11, each individual curve comprises three exotherms arising from the formation of the first polystyrene block, second polybutadiene block, and third polystyrene block. The amount of polar modifiers has a profound effect on the third exotherm. Because this exotherm depends on the rate of the third block formation, which is proportional to the first order of the already crossovered chain ends, it is clear from Figure 11 that higher modifier content results in a faster crossover. Similar observations were also obtained from the GPC analyses of the final SBS polymer as shown in Table IV. A larger amount of modifiers would enhance the crossover efficiency, which would otherwise result in a higher polydispersity. As shown in Table IV, the polydispersity decreases with an increase in the concentration of THF. The results clearly indicate that at a THF concentration of 4000 ppm, the crossover deficiency is minimal.

Effect of Modifiers on Coupling Efficiency When SBS Is Made Via Coupling Method

A typical GPC curve for a SBS copolymer made via the coupling method is shown in Figure 12 with peak

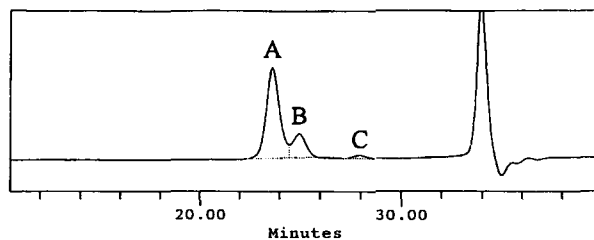


Figure 12 A typical GPC curve for SBS polymer made via the coupling method.

A, B, and C representing SBS, SB diblock, and polystyrene, correspondingly. The coupling efficiency is defined as

coupling efficiency

$$= \frac{\text{area of peak A}}{\text{area of peak A} + \text{area of peak B}}$$

The use of DBE as the coupling agent was complicated by the fact that the lithium-halogen exchange occurred between the alkyllithium and the haloalkane. Therefore, DBE, with 25% in excess of the stoichiometry amount, was charged to maximize the degree of coupling. As can be seen in Figure 13, the addition of the polar structure modifier exerts a significant impact on the coupling efficiency. The results clearly indicate the existence of an upper limit to the quantity of modifier. The coupling efficiency decreases at ~ 1 wt % THF concentration. THF, being a polar modifier, enhances the reactivity of the polymeric chain ends, but too much of it could result in extensive chain end complexation. In addition, the steric hindrance concomitant with the increase in vinyl content could also hinder the coupling process. In the absence of conclusive data, however, this argument must remain speculative.

The temperature dependence of the coupling efficiency is shown in Figure 14 for a set of experiments conducted in the presence of 4000 ppm THF. Coupling efficiencies as high as 78–82% were achieved at the optimal coupling temperature of 50–70°C. A further increase in the coupling temperature would incur a significant thermal deactivation causing a drop of coupling efficiency. In all the experi-

Table IV SBS Copolymers Made Via Sequential Polymerization

Polar THF (ppm)	500	2000	4000	500	2000	4000
Step 3 temp. (°C)	40	40	40	70	70	70
Polydispersity	1.122	1.075	1.056	1.136	1.129	1.037

Percent solids = 16.6%; *n*-BuLi [I] = 1.9×10^{-3} mol/L; styrene [M] = 0.37 mol/L; butadiene [M] = 1.68 mol/L.

ments, the linking process lasted 30 min, with 97% of the coupling completed in 10 min.

CONCLUSIONS

The efficiency of THF, functioning as a structure modifier for the polydiene segment of the SBS copolymer, was studied by analyzing the vinyl-1,2, *trans*-1,4, and *cis*-1,4 contents using ^{13}C -NMR. The vinyl content increased from 20 to 64% with an increase in the amount of THF from 200 ppm to 1 wt %, while the contents of *trans*-1,4 and *cis*-1,4 units decreased. The rate of styrene polymerization increased with an increase in THF concentration from 500 to 4000 ppm and then decreased when THF was further increased. Similarly, the rate of butadiene polymerization increased when THF concentration was increased from 500 ppm to 1 wt %, and then decreased when THF was further increased. Polymerization at a THF concentration of 4000 ppm–1 wt % resulted in the highest SBS polymerization rate with 55–65% 1,2-polybutadiene (vinyl) isomeric microstructure. In addition, for SBS polymer synthesized via a sequential process, the use of THF as the structure modifier enhanced the crossover efficiency, which would otherwise result in a skewed molecular weight distribution with a higher polydispersity. For SBS polymer made via a coupling process, the coupling efficiency decreased when the amount of THF exceeded approximately 1 wt %. The highest coupling efficiency was achieved at a coupling temperature of 50–70°C.

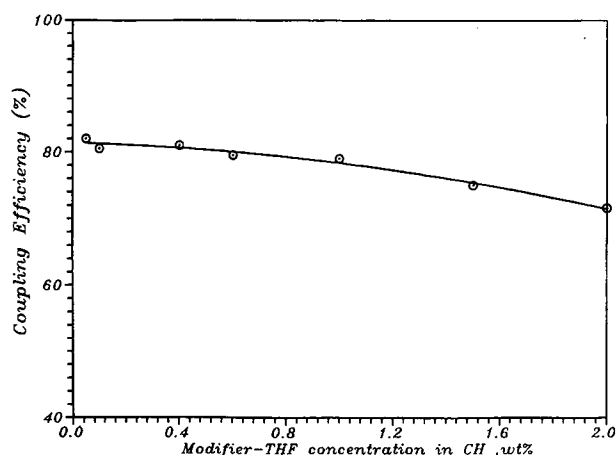


Figure 13 Effect of THF concentration on the coupling efficiency.

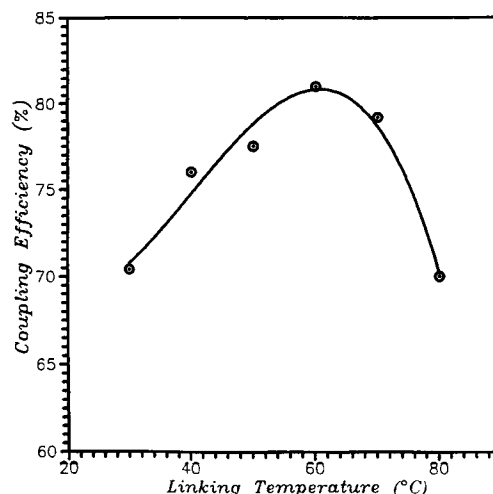


Figure 14 Effect of coupling temperature on the coupling efficiency.

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